Characterization of Interlayer Orientational Structures in Liquid Crystal Phases Using Resonant X-Ray Scattering

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Introduction: Resonant x-ray scattering has proven to be a unique method for measuring nm orientational periodicities in liquid crystal compounds. In particular, the interlayer orientational periodicities that occur in smectic-C* (SmC*) liquid crystal phases can only be observed when scattering at the resonance-edge of one of the atoms in the core of the liquid crystal molecule. Our resonant measurements on sulfur-containing compounds demonstrated that all the known variants of these tilted, layered SmC* phases can be described by a Clock Model. In this model, the azimuth of the molecular tilt direction varies between layers by the fixed amount $[2\pi/\nu + 2\pi\varepsilon]$ where ν is the number of layers in the superlattice while $\varepsilon << 1$ is the ratio of the layer spacing to a ~1μm optical pitch. Note that the low symmetry environment of the molecules hinders their rotation about their long axes resulting in a local spontaneous in-plane polarization perpendicular to the tilt plane of the molecules. Since this spontaneous polarization is coupled to the molecular tilt direction, the structure of the different SmC* variant phases will impact their electro-optic response. The composite helical structure of the Clock Model is predicted to exhibit two distinctive resonant x-ray scattering features: first, there are resonant satellite peaks at $Q_Z/Q_O = L + M\,[\,(1/\nu) + \varepsilon]$ where L, M are integers and M=0, ±1, ±2 and, second, for a σ-polarized incident beam, the M±1 resonant satellite peaks are π-polarized whereas the M±2 resonant satellite peaks are σ-polarized. In previous runs [1], the 1st and 2nd order satellite peaks were observed and their predicted polarization states confirmed for the antiferroelectric (AF) SmC_A* phase which has a two layer (ν=2) superlattice; for the ferrielectric SmC_{FI2}* phase which has a 4-layer (ν=4) superlattice; for the $SmC\alpha$* phase which has an incommensurate superlattice periodicity; and for the ferroelectric SmC* phase itself. In addition, a ferrielectric phase with a 3-layer superlattice, the SmC_{FI1}* phase, was observed but only its first order satellite peaks could be measured.

Results: During the period covered by this Activity Report, the 2nd order satellite peaks in the SmC_A* and $SmC\alpha$* phases were observed and the polarization state of the 2nd order satellite peaks in the SmC_A* phase shown to be σ-polarized as predicted. These observations provided additional support for the Clock Model. Moreover, a long pitched ferroelectric SmC* phase was confirmed to exist between the short-pitched $SmC\alpha$* and SmC_{FI2}* phases. The existence of this unexpected sequence of phases will be an important challenge for theorists modeling the phase transition sequence. Finally, although the Clock Model describes the observed resonant diffraction features, the Clock Model structures are intrinsically uniaxial whereas optical observations indicate that the ferrielectric phases are biaxial. A way to resolve the conflicting x-ray and optical results is to introduce distortions to the clock rotation, these distorted clock structures would give rise to additional resonant peaks. However, for long-pitched phases, these additional peaks would be irresolvable close to existing resonant peaks. Another distinctive feature is that the ratio of intensities for the second to the first order satellite peaks would be proportional to the cosine squared of the distortion angle. The peak intensity ratios of the resonant satellite peaks were carefully measured and shown to indicate a distortion angle consistent with that indicated from ellipsometry measurements [2].

Future Directions: We have recently obtained a high chirality dopant molecule. Optical characterization of mixtures of our sulfur compounds with the high-chirality dopant have indicated both shorter pitches as well as extended temperature ranges for the various SmC* phases. Since the spacing of the extra peaks in the *distorted* clock structures from peaks in the *undistorted* clock structures is inversely proportional to the pitch, the shorter pitched phases will enhance our ability to detect the extra peaks. Moreover, we will use a factor of two higher instrumental resolution to help resolve these features.

References: [1] P.Mach, et al., “Structures of chiral smectic-C mesophases revealed by polarization analyzed resonant x-ray scattering”,Phys. Rev. E**, 60**, 6793,1999.
[2] P.M.Johnson, et al., “The structure of the ferrielectric liquid crystal phases as determined by ellipsometry”, accepted for publication by Phys. Rev. Lett.